

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 092 397
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **83302135.5**

(51) Int. Cl.³: **C 22 C 19/05**

(22) Date of filing: **15.04.83**

(30) Priority: **20.04.82 US 370280**

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(43) Date of publication of application: **26.10.83**
Bulletin 83/43

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(84) Designated Contracting States: **AT BE DE FR GB IT SE**

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(54) **Nickel-chromium-molybdenum alloy.**

(57) A nickel-chromium-molybdenum alloy having high strength and resistance to corrosive environments such as are found in sour gas wells. Preferred alloys have good tolerance to the temperatures of the order of 300°C found in deep wells, are cold workable and have good ductility.

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Nickel-chromium-molybdenum alloy

The present invention relates to nickel-chromium-molybdenum alloys of high yield strength and resistance to corrosion in environments such as are found in sour gas wells.

5 A number of forms of corrosion come into play in sour gas well production. Typically sour gas wells contain hydrogen sulphide, carbon dioxide, methane and brine, often at operating temperatures of 250 to 300°C. Thus the most important forms of corrosion and
10 failure of well tubing are hydrogen sulphide stress cracking (HSSC) resulting from H_2S evolution, chloride stress corrosion cracking (CSCC), pitting and general corrosion. Well aging may also be a cause of early failure. Hydrogen sulphide stress cracking appears to
15 result from the presence of both H_2S and brine causing hydrogen evolution. This permeates the tubing causing "hydrogen embrittlement" which with tensile stress leads to cracking. The susceptibility of low alloy steels prevents their prolonged use in sour gas wells. Chloride
20 stress corrosion cracking, from release of chloride ions is particularly troublesome at higher operating temperatures, and the susceptibility of stainless steels to this form of corrosion prevents their use in sour gas wells. Pitting corrosion is also caused by chloride
25 attack, and is a particular problem for thin wall tubing. General corrosion causes weight loss of metal affecting the ability of the material to sustain load and its pressure bearing capabilities. Well aging is the time-dependent degradation in properties during prolonged
30 exposure at elevated temperatures, of 250° or even 300°C found in some wells. This affects the ability of the alloy to resist growth propagation.

 An alloy for use in sour gas wells, particularly those greater than 15,000 feet deep must

offer both resistance to the hostile corrosive environment and high yield strength, to allow the use of thin wall tubing allowing high volume gas flow but resisting tensile failure under high axial loading.

- 5 The alloys must be cold workable to generate the strength required necessitating a high level of work hardening. Also required is an acceptable level of "residual ductility", the ductility remaining after cold working, since considerable distortion is likely to be encountered
10 in sour gas well tubing in service. The alloy also needs hot workability and the ability to be fabricated.

The present invention is based on the discovery that certain Ni-Cr-Mo alloys can be produced satisfying these requirements even at applied stresses
15 in excess of 1000 MN/m².

- According to the present invention is provided a wrought alloy having a yield strength in excess of 1000 MN/m² and resistance to corrosive environments such as those found in a sour gas well having the composition
20 by weight 15 to 30% chromium, 5 to 15% molybdenum the total content of chromium and molybdenum being in the range 29 to 40%, 5 to 15% iron the total content of iron, chromium and molybdenum being not in excess of 46%, carbon up to 0.06%, up to 1% aluminium and/or titanium, up to
25 1% silicon, up to 0.5% niobium, less than 0.3% manganese balance nickel apart from incidental elements and impurities. Such alloys exhibit a high degree of resistance to hydrogen sulphide stress cracking, chloride stress corrosion cracking, pitting and general corrosion, and
30 have good ductility and resistance to "well aging".

It is particularly important that phosphorous and sulphur levels be kept as low as possible. Whilst manganese may be present up to 0.3%, it is preferably kept below 0.2%. Incidental elements may include copper
35 which is not required and may be kept to low levels, and cobalt up to about 25%. Boron up to 0.1% and mischmetal up to 0.1% may provide useful refining

additions. Carbon, while virtually unavoidably present, affects ductility. Magnesium and zirconium can be used for grain refinement. Tungsten does not offer any particular advantage, given its density and added cost. The carbon content is preferably held to not more than 0.03%, and amounts up to about 0.1% of magnesium and/or zirconium may be present.

It is important that alloys of the invention have correct compositional balance since otherwise premature failure may result. Preferably the chromium level does not fall below 20% to provide sufficient pitting resistance and HSSC and CCCC resistance. The chromium need not exceed 30%. When chromium levels of below 15% are used it is necessary to provide high levels of molybdenum and this can affect working characteristics.

Molybdenum markedly contributes to corrosion resistance but imparts a large degree of work hardening. Levels as low as 5% may be used in comparatively less severe conditions of temperature and pressure but levels of 7% or more are preferred. The content of chromium plus molybdenum should preferably be above 32% but preferably does not exceed 40%. This is because alloy brittleness, and other hot working problems can be caused at such levels. Also above 15% of molybdenum, the ductility of the alloy may be affected. The preferred content of molybdenum is 7 to 12%. The content of chromium and molybdenum also affects residual ductility. It has found to be desirable that the quantity % Cr - 2 (% Mo) is from 2 to 12 provides for optimum residual ductility.

Iron is present in alloys of the present invention at levels of from 5 to 15%, more preferably 8 to 12%. Excessive iron may produce unwanted morphological phases, such as sigma, and to prevent this the sum of molybdenum, chromium and iron is preferably below 46%.

Aluminium and titanium may be used as refining additions, and they contribute to workability. Preferably

alloys for use in the present invention contain 0.05 to 0.5% of either or both of these elements. The presence of silicon may not be deleterious, but it is preferably kept below 0.5% to avoid affecting the hydrogen stress cracking resistance.

Thus the preferred wrought alloy of the present invention having a yield strength in excess of 1000 MN/m² and intended for use in corrosive environments such as sour gas wells, consists of, by weight, 20 to 30% chromium, 7 to 12% molybdenum, the sum of chromium plus molybdenum being in the range 29 to 40%, the quantity of % chromium less twice the % molybdenum being in the range 2 to 12%, from 5 to 15% iron, the sum of chromium, molybdenum and iron not exceeding 46%, from 0.05 to 0.5% of either or both of aluminium and titanium, up to 0.06% carbon, up to 0.5% niobium, up to 0.5% silicon, up to 0.2% manganese the balance apart from impurities being nickel.

Alloys for use in the present invention, including the preferred alloys, are solution annealed at temperatures in the range 1066 to 1177°C, preferably 1093 to 1177°C for 0.5 to 5 hours, normally 1 to 2 hours. The alloys are cooled, for example by air cooling and are cold worked in the range 40 to 50% or more to provide yield strengths of the order of 1200 MN/m² or more. Since only low levels of aluminium and titanium are present the alloys are not age-hardenable, so that aging treatments are not required.

Some examples will now be described.

Example 1

A range of alloys both inside and outside the invention were produced in approximately 45 kg heats by induction melting high purity charge materials,

hot rolling the ingots to plate stock approximately
15 mm thick, and solution annealing followed by cold
rolling to develop strength. The amount of cold
rolling was varied. Test specimens were machined
5 from the cold rolled material normally in the trans-
verse direction. Tables I sets out the chemical
composition of the alloys and includes alloys in
which major element concentrations were varied, and
alloys based nominally on Ni-25% Cr - 10% Mo in which
10 minor element concentrations were varied.

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TABLE I

CHEMICAL COMPOSITIONS

	Alloy	Cr	Mo	Fe	C	Al	Ti	Other
5	A	14.7	9.8	6.2	.023	0.16	0.10	--
	B	14.7	9.9	10.7	.021	0.10	0.10	--
	C	9.9	9.7	11.0	.035	0.15	0.09	--
	D	15.0	4.8	11.1	.035	0.09	0.10	--
	E	14.2	16.0	10.3	.069	0.15	0.23	--
10	F	26.7	11.0	0	.020	0.18	0.07	1.9Nb
	G	18.7	2.8	16.9	.001	0.11	0.12	3.0Nb
	H	18.8	7.9	16.8	.007	0.11	0.11	3.1Nb
	J	27.8	9.8	0	.011	0.06	0.01	2.1Nb
	K	24.7	10.1	0	.034	0.25	1.40	3.1Nb
15	L	14.9	9.7	10.4	.031	0.11	0.09	2.7Nb
	M	19.8	20.3	11.4	.024	0.10	0.05	--
	N	24.7	20.7	10.3	.023	0.10	0.05	
	O	21.1	25.5	10.8	.035	0.09	0.04	
	P	26.5	15.7	11.9	.018	0.16	0.10	
20	S	24.6	10.0	9.1	.005	0.05	0.05	.22Si + .63Mn
	T	24.7	9.6	10.1	.120	0.05	0.06	--
	U	28.0	10.3	16.0	.005	0.08	0.06	
	V	24.9	10.0	10.1	.025	0.06	0.05	0.45Mn
	W	24.9	10.0	10.1	.025	0.06	0.05	0.95Mn
25	X	25.7	9.8	0	.030	0.17	0.10	
	1	19.4	10.1	10.8	.032	0.09	0.10	
	2	19.4	14.1	9.5	.031	0.14	0.08	
	3	23.8	9.8	9.4	.034	0.16	0.07	
	4	29.1	8.3	9.6	.070	0.17	0.08	
30	5	18.7	14.5	13.9	.003	0.09	0.09	
	6	23.8	10.7	10.3	.020	0.05	0.08	.016P
	8	24.6	10.0	9.1	.005	0.05	0.05	--
	9	24.7	9.6	10.1	.005	0.05	0.06	--
	10	24.7	9.6	10.1	.067	0.05	0.06	--
35	11	24.3	9.4	10.5	.027	0.11	0.09	.012Mg
	12	24.3	9.4	10.5	.027	0.11	0.09	.012Mg + .08Zr
	13	23.8	10.7	10.3	.020	0.05	0.08	.007P
	14	24.9	10.0	10.1	.025	0.06	0.05	0.20Mn
	15	24.8	10.1	10.1	.010	0.06	0.06	0.23Si
	16	24.8	10.1	10.1	.010	0.06	0.06	1.10Si
	17	24.9	10.3	10.1	.007	0.15	0.18	--
	18	24.9	10.3	10.1	.007	0.35	0.34	--
	19	24.9	10.3	10.1	.007	0.51	0.48	--
	20	23.4	9.6	10.0	.021	0.08	0.05	--
	21	23.4	9.6	10.0	.021	0.08	0.05	3.3W
	22	24.6	10.6	9.9	.003	0.12	0.12	.018P
	23	24.6	10.6	9.9	.003	0.12	0.12	.018P + .024B

It will be observed that alloys 1 to 6 and 8 to 23 are alloys of the present invention and alloys A to X are outside the present invention. Alloys 8 to 23 are the preferred alloys of the invention.

5 The specimens were subjected to H₂S stress corrosion tests (NACE Spec. Standard TM-01-77) in a solution of 5g glacial acetic acid and 50g NaCl in 945g H₂O saturated with H₂S gas. This allows sensitivity to H₂S gas at ambient temperatures to be
10 tested.

The specimens were 3-point bent beam samples loaded in small electrically insulated test fixtures stressed to various percentage of the yield strength, usually 100%. The cold rolled materials were given
15 "well aging" heat treatments at 260°-315°C for various times before testing. The samples were oriented in the transverse direction from the cold worked plate.

(Note: extra specimens were first deformed to determine the load-deflection characteristics.) Specimens for
20 test were then loaded in the fixtures to predetermined deflection corresponding to desired stress levels. Some U-bend specimen were also tested. All samples were attached to small pieces of steel to provide galvanic coupling.

25 Yield strength (0.2% offset), applied stress level and HSSC results are given in Table II. As noted duplicate samples were tested, the test period covering five (5) weeks.

30 Additional results are reported in Table III involving U-bend tests in the NACE H₂S solution, the test period being varied as indicated.

TABLE II
RESULTS OF NACE H₂S STRESS CORROSION TEST
THREE POINT LOADED NOTCHED BEAM SAMPLES
COUPLED TO IRON DUPLICATE SAMPLES EXPOSED 5 WEEKS

	<u>Alloy</u>	<u>Yield Strength</u> <u>MN/m²</u>	<u>Applied Stress Level</u> <u>(% of Yield Strength)</u>	<u>Results of</u> <u>SCC Test</u>
5	A	1565	80	F
	B	1524	80	F
	B	1524	60	F
	C	1462	60	P
	D	1317	80	F
	G	1103	100	F
	H	1200	100	P
	J	1193	100	P
	Q	1641	80	P
	Q	1145	100	F
	T	1241	100	P
	V	1138	100	P
	W	1014	100	P
10	1	1000	100	P
	2	1276	100	P
	3	1241	100	P
	4	1255	100	P
	5	1172	100	P
	6	1186	100	P
	9	1158	100	P
15	10	1234	100	P
	13	1165	100	P
	18	1069	100	P
	19	1062	100	P
	20	1131	100	P
	21	1117	100	P
	23	1165	100	P

P = Passed

F = One or Both Samples Failed in 5 Weeks or Less

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TABLE III

U-BEND TEST RESULTS IN NACE H₂S SOLUTION

	<u>Alloy</u>	<u>Outer Fibre Stress of U-Bend MN/m²</u>	<u>Time to Failure (days)</u>	
5	F	1214	21,	21
	S	1207	63+,	63+
	T	1317	63+,	63+
	V	1220	63+,	63+
	W	1193	63+,	63+
10	1	1186	63+,	63+
	2	1351	21,	21
	3	1324	21,	63
	6	1310	63+,	63+
	7	1124	21,	63+
	8	1151	63+,	63+
15	9	1282	63+,	63+
	10	1317	63+,	63+
	13	1289	63+,	63+
	16	1193	21,	21
20	17	1234	63+,	63+
	18	1151	63+,	63+

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Example 2

Some U-bend specimens of the alloys of Example 1 were loaded with bolts made of alloy C276 in a hydrogen sulphide saturated solution containing 25% NaCl, 0.5% acetic acid and 1 g/l elemental sulphur, at various temperatures in the manner described in the Society of Petroleum Engineers AIME, Paper No. SPE 9240, 1980 by Vaughn and Greer. Results obtained are indicated in Table IV.

TABLE IV
RESULTS OF CHLORIDE STRESS CORROSION TESTS

	<u>Alloy</u>	<u>Test Temp. (°C)</u>	<u>Time of Failure (days)</u>	<u>Outer Fibre Stress of U-Bend MN/m²</u>
15	A	204	36+	710
	B	204	36+	745
	C	204	36+	696
	D	204	36F	607
	E	232	46F	1220
	F	288	173+	1234
	G	288	80F	1131
	H	288	28F	1207
20	J	288	173+	1276
	K	288	62F	1310
	L	288	28F	690
	Q	204	36+	745
	R	204	36+	641
	S	288	93+	1282
	U	204	36+	634
	W	288	31+	1193
25	X	232	223F	1434
	1	204	36+	745
	2	288	135+	1103
	3	288	107F	1048
	4	288	76F	1158
	5	288	206+	1131
	6	232	107+	1296
	8	288	93+	1193
30	9	288	93+	1282
	11	288	93+	1255
	12	232	107+	1248
	13	232	107+	1289
	14	288	31+	1234

U-Bend Specimens; F = Sample Failed, + = No Failure

Example 3

Some specimens of the alloys of Example 1 were totally immersed in a 6% ferric chloride solution at about 50°C for 72 hours as described in ASTM Standards Part 10, Section G. (Good correlation between pitting behaviour in ferric chloride and behaviour in sour gas well environments has been observed in the literature).

Electrochemical tests were conducted at 60°C in 10,000 ppm NaCl solution adjusted to pH 2 with hydrochloric acid. Scans were run at 60 v/hr to characterize the pitting resistance. The current density during the forward scan at +0.6 v vs. standard calomel electrode was used as a measure of the pitting behaviour as described by P.E. Morris and R.C. Scarberry, Corrosion, Vol. 28, 1972, p. 444. Data is reported in Table V. The results obtained are given in Table V.

TABLE V
PITTING TEST RESULTS

	Alloy	Surface Appearance After 15 Days in Test at 204°C	Ferric Chloride Weight Loss (g/m ²)	Current Density at +0.6V in 10 ⁴ ppm Cl (μA/cm ²)
20	A	Fair	--	2,100
	B	Fair	--	2,500
	C	Poor	1,175	6,400
25	D	Fair	--	8,000
	Q	Good	--	640
	R	Poor	1,836	8,000
	T	--	71	--
	U	Good	--	420
	V	--	0.707	--
	W	--	0	--
30	X	--	--	285
	1	Moderate	--	1,080
	2	--	0.477	--
	3	--	0.365	--
	6	--	0	--
	9	--	0.812	--
	10	--	111	--
35	14	--	0	--
	15	--	0	--
	16	--	0.353	--

Example 4

In order to assess the work hardening rate, the true stress-strain behaviour of a number of alloys of Example 1 was determined by tensile tests in which load and sample diameter were determined periodically up to fracture. The results obtained are given in Table VI.

TABLE VI
WORK HARDENING BEHAVIOUR
TRUE STRESS VALUES AFTER A
TENSILE TRUE STRAIN OF 0.4

<u>Alloy</u>	<u>Flow Stress</u> <u>MN/m²</u>
A	1241
B	1269
C	1158
D	1069
U	1062
1	1220

Example 5

The "residual ductility" of a number of alloys of Example 1 was assessed by measuring the strain to fracture minus the strain to work harden the alloys to a stress of 1241 MN/m². The values shown in Table VII are a measure of the ductility remaining after cold working to a yield strength of 1241 MN/m².

TABLE VII
RESIDUAL DUCTILITY, TRUE STRAIN TO FAILURE MINUS
TRUE STRAIN TO PRODUCE A TRUE STRESS OF 1241 MN/m²

	<u>Alloy</u>	<u>Residual Ductility</u>
5	B	0.43
	C	0.36
	D	0.61
	Q	0.38
	R	0.79
10	1	0.41
	11	0.75
	12	0.89
	13	0.93

In terms of residual strain, a number of alloys outside the invention did exhibit a sufficient degree of ductility subsequent to cold working. Alloy D is such an alloy. Alloy 1 is a marginal composition. Moreover, it does not satisfy the relationship $\% \text{Cr} - 2 (\% \text{Mo})$ is in the range 2 to 12. Given the numerous alloys within the invention and which are characterised by a highly satisfactory combination of properties, including residual ductility, Alloy 1 would not be recommended for sour gas well applications. Alloys 11, 12 and 13 were excellent.

From the foregoing examples 1 to 5 it will be observed that alloys for use in the present invention gave quite good results. This is not true of the comparative alloys. It will be observed that no tests were carried out on alloys M, N, O and P which all cracked during hot working. This is a result of their high molybdenum or molybdenum plus chromium levels. Results on comparative commercial alloys from the literature suggest that alloy C273, MP-35-N and alloy 625 all crack in NACE H₂S U-bend tests within a week or two. Some of the alloys of the invention subjected to these tests survived at stress levels of over 1200 MN/m², and did well at temperatures of 288°C. Commercial

alloys fail rapidly under such conditions.

Example 6

In order to ascertain what problems might evolve if commercial size ingots were made, four simulated heavy section castings were prepared. These were produced as 136 kg heats that were cast into 20.3 cm x 20.3 cm x 35.6 cm sand-moulds with exothermic hot tops. The castings approximate the solidification that would take place in ingots of the order of 0.09 m² in cross sectional area.

The nominal chemistries of the ingots are given in Table VIII:

TABLE VIII

	<u>Alloy</u>	<u>Cr</u>	<u>Mo</u>	<u>Fe</u>	<u>Ni</u>
15	24	25	10	10	bal.
	X	28	10	10	bal.
	Y	25	13	10	bal.
	Z	25	10	15	bal.

Metallographic examination of cross-sections from the ingots showed only traces of amounts of second phase particles in Alloy 24, but significant amounts of second phases in the other alloys. Slices from all four castings were successfully hot rolled at 1149°C from 2.54 cm to 1.27 cm thickness with no signs of cracking. No second phase particles were seen in the hot rolled Alloy 24, but significant amounts were still present in X, Y and Z. The chemistries of the latter alloys were too rich in Cr + Mo + Fe. This total sum should be maintained at a level not greater than about 46.

As well as being useful in deep sour gas wells, the alloys described hereinbefore can be used in other corrosive environments in which high strength is required. Such applications include, intermediate gas wells, aqueous and marine environments, scrubbers, chemical plant equipment (such as tubing and piping), aircraft and aerospace and applications. Mill product

forms include forgings, bar plate, extrusions and sheet.
Among other structural shapes might be mentioned
fasteners, valves, pins, shafts and rotors.

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Claims

1. A wrought alloy having a yield strength in excess of 1000 MN/m² and resistance to corrosive environments such as those found in a sour gas well characterised in that it consists by weight of 15 to 30% chromium, 5 to 15% molybdenum, the total content of chromium and molybdenum being in the range 29 to 40%, 5 to 15% iron, the total content of iron, chromium and molybdenum being not in excess of 46%, up to 0.06% carbon, up to 1% aluminium and/or titanium, up to 1% silicon, up to 0.5% niobium, less than 0.3% manganese balance nickel apart from incidental elements and impurities.
2. A wrought alloy for use in corrosive environments such as sour gas wells, having a yield strength in excess of 1000 MN/m² characterised in that it consists by weight of 20 to 30% chromium, 7 to 12% molybdenum, the sum of chromium plus molybdenum being in the range 29 to 40% the quantity of % chromium less twice the % molybdenum being in the range 2 to 12%, from 5 to 15% iron, the sum of chromium, molybdenum and iron not exceeding 46%, from 0.05 to 0.5% of either or both of aluminium and titanium, up to 0.06% carbon, up to 0.5% niobium, up to 0.5% silicon, up to 0.2% manganese the balance apart from impurities being nickel.
3. An alloy as claimed in claim 1 or claim 2 in which the alloy contains from 23 to 27% chromium and 7 to 12% molybdenum and in which the sum of chromium plus molybdenum is in the range 31 to 38%.
4. An alloy as claimed in any of claims 1 to 3 in which the carbon content of the alloy does not exceed 0.03%.
5. Use of a wrought alloy as claimed in any preceding claim in a sour gas well environment.

6. A method of producing a wrought product having a yeild strength in excess of 1000 MN/m² for use in corrosive environments comprising melting an alloy of the composition claimed in any one of claims 1 to 4, solution annealing the alloy in the temperature range 1050 to 1200°C, cooling and cold working the alloy to develop the desired strength.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application number

EP 83 30 2135

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	FR-A-1 309 587 (BASE) * Whole document *	1	C 22 C 19/05
X	FR-A-2 416 956 (CABOT CORP.) * Claims 1,2,7,8 *	1,4,5	
X	FR-A-1 536 741 (UNION CARBIDE CORP.) * Abstract, points 1,2 *	1,4	
A	DE-A-2 929 811 (HITACHI) * Claim 1, last paragraph *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 22 C 19/05
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29-07-1983	Examiner LIPPENS M.H.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			